

SUMMARY OF SAMPLE-COLLECTION AND SAMPLE-PROCESSING PROCEDURES FOR SPECIFIC ANALYTES

5.6

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Collection methods, equipment needs, and preservation requirements for specific analytes can change over time, owing to advancements in knowledge and technology. Any major changes to sample collection and processing procedures will be announced on the USGS Office of Water Quality Web site (<http://water.usgs.gov/lookup/get?owq/>) or as a technical memorandum (<http://water.usgs.gov/lookup/get?techmemo/>). Consult NWQL or the District water-quality specialist for instructions related to the collection, processing, or analysis of solid materials, gases, biota, and any other analytes not described in this manual. Chemical formulas used in this section are spelled out in "Conversion Factors, Selected Terms, Abbreviations, and Chemical Formulas."

COMMON ORGANIC COMPOUNDS

5.6.1

Sample bottles for organic-compound analyses are precleaned and baked at the laboratory and should be received capped. Collect and process samples within processing and preservation chambers, as appropriate, and while wearing disposable, powderless latex or nitrile gloves. In general, change gloves between each collection and processing step and with each new sample type. After collection and processing, check that the information is correct on the bottle label. Place the filled glass sample bottle in a foam sleeve and chill sample to 4°C or below without freezing.

- ▶ Most samples for organic-compound analysis are collected in 1-L amber glass bottles, leaving headspace in case of sample expansion (Appendix A5-A).

- ▶ Samples for glyphosphate analysis are collected in 40-mL vials, leaving headspace in case of sample expansion.
- ▶ Volatile organic compounds are collected in 40 mL baked glass vials without headspace.

Do not field rinse bottles prepared for organic-compound samples.

5.6.1.A Volatile Organic Compounds (VOCs)

Label baked 40-mL amber glass vials as "VOC." Collect three vials per sample for ground water and four vials per sample for surface water.

- ▶ **Do not use tape on the vials.** Tape causes the autosampler to jam.
- ▶ **Do not aerate the sample.** Samples with air bubbles must be discarded.

TECHNICAL NOTE: Some programs, such as NPDES and NAWQA, require treatment of VOC samples by adding HCl.

To determine the number of HCl drops needed to lower sample pH to ≤ 2 before collecting the sample, collect a test sample toward the end of purging and pour 40 mL of the sample into a beaker or spare VOC vial. Check the pH (use narrow-range pH indicator strips such as pHDrion™) after each addition of 2, 3, and 4 drops. Do not use pH indicator strips that are old or expired.

To collect VOC samples:

1. Insert the fluorocarbon polymer discharge line from the pump or the bailer emptying device to the bottom of the vial; flow should be smooth and uniform (between 100 and 150 mL/min).
 - If the vial was supplied with chemical treatment, do not fill vial to overflowing.
 - If no chemical treatment will be added or if the treatment will be added after the vial is filled, allow sample to overflow the vial in order to help purge air from the sample.
2. Slowly withdraw the discharge line from the bottle; slide the discharge line to the side of the vial as the line is about to clear the vial so as to avoid breaking the water surface. Leave a convex meniscus.

3. Add chemical treatment (HCl) to sample if required by the program and if the HCl is not already in the vial. Add 2 to 5 drops (see TECHNICAL NOTE above) of 1:1 HCl:H₂O, drop by drop, to the filled vial to lower the pH to ≤ 2 . Dispense the HCl from a fluorocarbon polymer dropper bottle. **Do not add more than 5 drops of HCl.**
4. If residual chlorine is present, add 25 mg of ascorbic acid to the vial in addition to the HCl.
5. Replace the vial cap immediately. Do not allow the samples to degas. The fluorocarbon polymer (white) side of the septum in the cap should contact the sample.
6. Invert the vial and tap the vial to release any bubbles. Check carefully for gas bubbles in the sample. If gas bubbles are present, discard the sample vial and resample. If degassing of the samples makes excluding bubbles impossible, record this on the field forms and the laboratory ASR form and report an estimate of the relative volume of bubble(s) in the sample.
7. Protect the sample from sunlight. Chill and maintain at 4°C or below without freezing.

Semivolatile Organic Compounds 5.6.1.B (Base-Neutral Acids), Pesticides, Organonitrogen Herbicides, Polychlorinated Biphenyls (PCBs)

Label 1-L baked glass bottles as "GCC." Add the laboratory code, if required. Certain analytical schedules require a filtered sample (check with the laboratory for processing and bottle requirements).

1. Fill to the shoulder of the bottle directly from the sampling, splitting, or filtering device.
2. Be sure to leave headspace in the bottle.
3. Chill and maintain at 4°C or below without freezing.

Instructions for field solid-phase extraction (SPE) of pesticides are provided in section 5.3. Field SPE is an alternative method for processing samples for pesticide analysis and should be considered in situations where transporting glass bottles, shipping weight, or holding/shipping times pose a problem. Field SPE samples usually are extracted after most other onsite activities are completed or by a third team member because equipment setup, sample extraction, and equipment cleaning can be quite time consuming.

5.6.1.C Phenols

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Label 1-L baked amber glass phenol bottle as "LC0052."

1. Fill the bottle with raw sample directly from the sampling or splitting device.
2. Leave a small headspace in the bottle.
3. Add 2 mL of 8.5 percent H_3PO_4 to a 1-L sample to achieve pH 4, and 10 mL of CuSO_4 to a 1-L sample (100 g/L).
4. Chill and maintain at or below 4°C without freezing.

5.6.1.D Carbon

Particulate organic and inorganic carbon¹⁰:

1. Label the samples for Total Particulate Carbon (TPC) as "LC2606" and for Particulate Inorganic Carbon (PIC) as "LC2608." Note that the concentration of Particulate Organic Carbon (POC, LC2611) is calculated as the difference between TPC and PIC.
2. Refer to the detailed instructions given in section 5.2.2.C for processing the TPC and PIC samples.

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Raw (TOC) sample:

1. Use 125-mL baked glass bottles. Label the sample for total organic carbon "LC114."
2. Pour, discharge, or pump the raw sample directly into the sample bottle, up to the shoulder of the bottle (leave headspace).

¹⁰The analysis for total particulate nitrogen (TPN), LC2607, is performed on the TPC sample upon request.

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Filtered (DOC) and suspended (SOC) samples:

1. Label the DOC sample as follows: (a) "LC2612" if processed through a Supor capsule filter; (b) "LC2613" is processed through a GF/F; and (c) "LC113" if processed through a silver filter.
2. Refer to the detailed instructions given in section 5.2.2.C for processing DOC using either the capsule or GF/F filtration procedures. Fill the 125-mL baked glass bottle to the shoulder—allow enough headspace for the addition of 4.5N H₂SO₄ and the expansion of the chilled sample. Refer to the instructions given in Appendix A5-D if using the silver-filter procedure.
3. Label the SOC sample as "LC305." Refer to the detailed instructions given in Appendix A5-D for the silver-filter procedure. LC305 is available only as a custom analysis.

Methylene Blue Active Substances (MBAS) and Oil and Grease **5.6.1.E*****MBAS:***

1. Label a 250-mL polyethylene bottle as "RCB."
2. Field rinse the bottle and fill with raw sample.
3. Chill and maintain at 4°C or below without freezing.

Oil and grease:

1. Label a 1-L baked amber glass bottle as "LC0127."
2. Do not field rinse; fill with raw sample, leaving a small headspace.
3. Add approximately 2 mL of sulfuric acid to reach a pH <2.
4. Chill and maintain at 4°C or below, without freezing.

MAJOR IONS AND TRACE ELEMENTS**5.6.2**

Bottles (including acid-rinsed polyethylene and glass bottles) used to collect samples for analysis of major ions and trace elements should be rinsed and partially filled with DIW before they are used at the field site, as instructed in NFM 3. Exceptions apply when collecting samples for analysis of isotopes or radiochemicals—consult the isotope laboratory. Collect and process samples within processing and preservation chambers, as appropriate, and while wearing appropriate (for example, vinyl) disposable, powderless gloves. In general, change gloves between each collection and processing step. After collection and processing, check the bottle label for correct information and place glass bottles into foam sleeves.

- ▶ Use acid-rinsed bottles (for cations) only if they arrive capped with colorless translucent caps. Do not use any acid-rinsed bottles that are received uncapped.
- ▶ Before going to the field, first rinse and then half fill each bottle with DIW as described in NFM 3.
- ▶ Discard DIW from bottles at the field site before field rinsing and (or) sampling.
- ▶ **Field rinse the inside of sample bottles and bottle caps with sample** (table 5-2; Appendix A5-B). Use filtrate to rinse the bottles that will contain filtered sample.

5.6.2.A Major and Minor Cations and Trace Elements

Use of Clean Hands/Dirty Hands techniques and good field practices are required for samples with parts-per-billion concentrations of trace elements and are recommended for all samples.

Raw samples:

1. Label acid-rinsed polyethylene bottles as "RA" for major and minor cations and most trace-element samples. Label bottles with the laboratory schedule, as appropriate.
 - Arsenic, antimony, and selenium analyses—Label bottles as "RAH." (Some samples are designated "USEPA"—check with the laboratory.)
 - Mercury samples—Label glass bottles as "RAM."
 - USEPA drinking water samples—Label bottles as described in NWQL Technical Memorandum 97.05 or as directed.
2. Field rinse and fill sample bottles directly from the sample-collection or processing device.
3. Add chemical treatment, as specified by the analyzing laboratory.
 - Major and minor cations and trace elements: Add HNO_3 to lower sample pH to <2.
 - Mercury: Add contents of vial containing 2 mL of 6N ultrapure HCl.

Filtered samples:

1. Label acid-rinsed polyethylene bottles as "FA" for most trace-element samples, including arsenic, antimony, and selenium. Check NWQL Technical Memorandum 97.05 for requirements for USEPA drinking water samples.

Exception: Mercury—Label the acid-rinsed 250-mL glass bottles as "FAM."
2. Field rinse and fill sample bottles directly from the filter assembly. Refer to section 5.2 for filtration instructions.

3. Add chemical treatment, if specified by the analyzing laboratory.
- Major and minor cations and trace elements: Add HNO_3 to lower sample pH to <2 .
 - Mercury: Add contents of vial containing 2 mL of 6N ultrapure HCl.

Nutrients (Nitrogen and Phosphorus) 5.6.2.B

Refer to Office of Water Quality Technical Memorandums 94.16, 99.04 and 2000.08 for the most recent changes to collecting and processing nutrient samples. See 5.6.1.D and 5.2.2.C for processing of a Total Particulate Nitrogen (TPN) sample, LC2607.

Raw samples:

1. Label bottles as follows:
 - "WCA" for raw samples to be treated with H_2SO_4 (125-mL translucent bottles are preferable).
 - "ERC" for raw samples collected for the USEPA Drinking Water Program (refer to National Water Quality Laboratory Technical Memorandum 97.05 or contact the laboratory for instructions).

A clean, graduated cylinder may be used when the volume of sample to be filtered is less than 64 mL.

2. Field rinse and fill the sample bottles directly from the sampler or sample splitting device.
3. Add a chemical treatment to WCA and ERC samples, as appropriate.
4. Chill WCA and ERC samples immediately and maintain at 4°C or below without freezing.

Filtered samples:

1. Label bottles as follows:
 - FCC" for filtered samples (125-mL brown bottles).
 - FCA" for filtered samples to be treated with H_2SO_4 (125-mL brown bottles).
2. Field rinse and fill sample bottles directly from the capsule filter or other filter assembly.

- **Use of 0.45- μ m pore-size filter media is the standard to date for State or Federal programs that regulate drinking water and for routine water-quality studies for which consistency with historical nutrient data is necessary.** +
 - Use of 0.2- μ m pore-size filter media is recommended for studies for which exclusion of bacteria from the sample is desirable, and inconsistency with historical data is not an issue. Prefilter sediment-laden samples through 0.45- μ m filter media. Record the filter pore size used, if other than 0.45 μ m, under the comments section on the field form and ASR forms.
3. Add chemical treatment to FCA samples. (FCC samples do not require chemical treatment.)
 4. Chill FCC and FCA samples immediately and maintain at 4°C or below without freezing.

5.6.2.C Anions

Label polyethylene bottles as "FU" (filtered untreated). Process alkalinity samples for field titration using the same steps as for other anions (with the exception of ANC samples) (NFM 6).

1. Refer to section 5.2 for filtration instructions. +
2. Field rinse and fill sample bottles directly from the capsule filter (or filter assembly).
3. Do not add chemical treatment.

Exceptions:

- **Cyanide**—Label the 250-mL polyethylene bottle as "LC0880" for filtered sample and as "LC0023" for raw sample. **Cyanide requires addition of NaOH to raise the pH to >12.**
- **ANC** (acid neutralizing capacity)—Do not filter the ANC sample. Label sample bottle as "RU" (NFM 6).

TABLE ISOTOPES AND RADIOCHEMICALS 5.6.3

Isotopes and radiochemicals generally are not processed in a processing or preservation chamber, unless samples are being handled in a glove box. Wear appropriate, disposable, powderless gloves when collecting and processing samples.

Leave enough air space (at least 2 cubic centimeters) if glass bottles are used and the sample will be chilled to allow for the expansion of water samples unless instructed otherwise (Appendix A5-C). Close the polyseal cap tightly and seal with wax or plastic tape, or as directed below for the specific isotope or radiochemical.

Carbon ($^{13}\text{C}/^{12}\text{C}$ and ^{14}C) 5.6.3.A

Do not let the sample contact air. Filter the sample along with other inorganic-constituent samples if particulates are visible. **Samples without particulates do not require filtration or chemical treatment** (NWQL Technical Memorandum 96.05). If ^{13}C will be collected by direct precipitation in the field using ammoniacal SrCl_2 , then the precipitates must be submitted as washed, dried, homogenized powders. **The laboratory will not accept bottles with ammoniacal SrCl_2 in solution.**

Samples for $^{13}\text{C}/^{12}\text{C}$ analysis:

1. Label a 1-L glass bottle as " $^{13}\text{C}/^{12}\text{C}$, RUS," and the laboratory code or schedule number (as requested by the laboratory).
2. Filter the sample if particulates are visible. Establish a closed path from the sample source through the filter and to the bottle to exclude air from the collection system.
3. When filling the bottle, fill from the bottom of the bottle and allow an overflow of two to three bottle volumes. Cap the sample immediately.

Samples for ^{14}C analysis:

The sample must provide a minimum of 5 mg dissolved inorganic carbon (DIC) per sample container. +

1. Label bottles as " ^{14}C , RUS/RUR," and the appropriate laboratory schedule number. Check with the laboratory and refer to NWQL Technical Memorandum 96.05 for bottling and other field requirements for samples to be analyzed for ^{14}C .
2. Collect sample in duplicate. Filter the sample if particulates are visible. Establish a closed path from the sample source, through the filter, to the bottle to ensure that air is excluded from the collection system.
3. Fill sample container.
 - For samples with ^{14}C content greater than or equal to 5-percent modern carbon, fill the bottle from the bottom of the bottle, allowing an overflow of 2 to 3 bottle volumes. This helps to purge air from the sample. Cap the bottle immediately. For potentially low ^{14}C concentrations, (<10 percent modern carbon) or if relatively long filtration time is required, flush the headspace above the water sample with nitrogen while filling the bottle.
 - For samples with ^{14}C content less than 5-percent modern carbon, use a stainless steel collection vessel, such as a WhiteyTM Sample cylinder No. 304L-HDF4, with stainless steel valves on each end. Flush with several liters of filtrate from the bottom of the cylinder up and close the cylinder, leaving no headspace. +
4. Archive a duplicate sample and store in the dark, chilled to 4°C or below without freezing.
 - Secure container caps with electrical tape.
 - Record the sample pH and alkalinity on the sample bottle.

Hydrogen ($^2\text{H}/^1\text{H}$) and Oxygen ($^{18}\text{O}/^{16}\text{O}$) 5.6.3.B

Hydrogen and oxygen isotope samples can be collected together in one bottle. Use either a 60-mL clean glass bottle or a 250-mL polyethylene bottle. Label the bottles as "RUS, SH 1142." Use caps with polyseal conical inserts. **To request bottles with appropriate caps, send E-mail to isotopes@usgs.gov.**

- Do not field rinse bottles.
 - Do not add chemical treatment.
 - Samples may be either raw or filtered.
1. Fill bottle to overflowing directly from the sampler or sample splitting device (raw sample) or from the capsule filter or other filter assembly (filtered sample).
 2. If filling a glass bottle, fill to overflowing and then decant the sample until the water level is at the bottle shoulder. Cap the bottle immediately.
 3. If filling a polyethylene bottle, fill to overflowing and cap the bottle immediately, leaving no headspace. Do not use polyethylene bottles if the sample will be held or archived.

5.6.3.C Nitrogen ($^{15}\text{N}/^{14}\text{N}$)

Collect filtered, untreated sample (**do not use mercuric chloride**) in a 1-L amber or foil-wrapped glass or high-density polyethylene bottle. Use a polyseal bottle cap. Refer to National Water Quality Technical Memorandum 95.05.

1. Label the bottles as "RUS" and with the appropriate laboratory code (LC 1717, for $^{15}\text{N}/^{14}\text{N}$ as ammonia; LC 1718, for $^{15}\text{N}/^{14}\text{N}$ as nitrate; or LC 1921, for $^{15}\text{N}/^{14}\text{N}$ as nitrate plus ammonia).
2. Fill the bottle to the shoulder directly from the capsule filter or other filter assembly.
3. Put the glass sample bottle into a foam sleeve and keep it chilled at or below 4°C without freezing. Ship overnight, per shipping instructions in NWQL Technical Memorandum 95.04.

5.6.3.D Sulfur ($^{34}\text{S}/^{32}\text{S}$)

Dissolved sulfide and sulfate are collected and processed separately, according to the directions given in Carmody and others (1998).

1. Label the bottles as "RUS" and with the appropriate laboratory code or schedule number.
2. Send questions to the following E-mail address: <isotopes@usgs.gov>. Special equipment, chemical reagents, and training are needed in order to collect these samples properly.

Sulfate: Procedures and equipment differ for processing the sulfate sample, depending on whether sulfate concentrations are less than 20 mg/L or equal to or greater than 20 mg/L. Onsite estimation of sulfate concentration is described in Carmody and others (1998).

- When a water sample from which dissolved sulfate will be collected for isotopic analysis also contains dissolved sulfide (greater than 0.01 mg/L), the sulfide should be removed by nitrogen stripping to avoid contamination of the sulfate sulfur by oxidized sulfide sulfur with very different isotopic composition.

- Sulfate in water with concentrations of greater than 20 mg/L sulfate is collected by precipitating BaSO_4 from an acidified sample (up to 2-L volume). BaSO_4 can be precipitated and filtered in the laboratory or in the field.
- Anion exchange resin can be used to collect sulfate from samples in which sulfate concentrations are less than 20 mg/L.

Sulfide: Determine if dissolved sulfide (H_2S) is present by its distinctive rotten-egg odor. Measure H_2S concentration with a field spectrophotometer.

- Measurement of dissolved sulfide concentrations greater than 0.6 mg/L with a field spectrophotometer has been problematic.
- An alternative method for samples with dissolved sulfide concentration greater than about 0.5 mg/L is to collect the dissolved sulfide by direct precipitation of Ag_2S by adding AgNO_3 to the sample. Care must be taken to add sufficient AgNO_3 to precipitate all the sulfide present, or the sulfide sample will be fractionated.
- A method for collection of dissolved sulfide by nitrogen stripping and precipitation of Ag_2S in an AgNO_3 trap has been tested and found to cause a small fractionation of the isotopic composition of the sulfide. Two approaches are recommended to minimize this fractionation: (1) collect sulfide by nitrogen stripping for 3 hours or more to minimize the amount of sulfide left in the carboy and, thus, the fractionation produced; and (2) determine the kinetic fractionation factor (α) for the collection apparatus and use this α to calculate the original sulfur isotopic composition of the dissolved sulfide in the ground water from Ag_2S collected for a short time (about 30 minutes).

5.6.3.E Radium 226 and Radium 228

Label acid-rinsed polyethylene bottle(s) as "FAR" and add the appropriate laboratory code ("LC 794" for radon-226 and "LC 1364" for radon-228). Bottle-size requirements depend on analytical method or schedule.

1. Filter the sample using the procedures for inorganic-constituent samples, and fill the sample bottle to the shoulder directly from the capsule filter or other filter assembly.
2. Add reagent-grade HNO_3 to preserve sample to $\text{pH} < 2$. **Do not substitute HCl for HNO_3 .**

5.6.3.F Uranium (U-234, U-235, U-238)

Label 1-L acid-rinsed polyethylene bottle(s) as "FAR, SH 1130." Check with the laboratory for bottle requirements for the analysis requested.

1. Filter the sample and fill the sample bottle to the shoulder directly from the capsule filter or other filter assembly.
2. Add reagent-grade HNO_3 to preserve the sample to $\text{pH} < 2$. **Do not substitute HCl for HNO_3 .**

5.6.3.G Gross Radioactivity

Label 1-L acid-rinsed polyethylene bottle(s) as "FAR" (filtered sample) for the gross alpha and the gross beta analyses and with the appropriate laboratory schedule number. The laboratory schedule requested depends on the concentration of total dissolved solids in the sample.

1. Filter the sample.
2. Fill the sample bottle to the shoulder directly from the capsule filter or other filter assembly.
3. Add reagent-grade HNO_3 to preserve the sample to $\text{pH} < 2$. **Do not substitute HCl for HNO_3 .**

Tritium 5.6.3.H

Label a 1-L bottle as "RUR" and add the appropriate laboratory code. (High density polyethylene bottles are preferred; a glass bottle with a polyseal cap may be used. Refer to National Water Quality Technical Memorandum 92.04.)

- Do not place tritium samples near watches or other devices with luminescent dials. Do not store sample near tritium sources (for example, glowing clocks, watches, signs).
 - **Do not field rinse sample bottles.**
1. Fill bottle with raw, untreated sample. The bottle should be dry before being filled. It might be desirable to flush the bottle with a filtered, inert gas such as argon or nitrogen before leaving for the field—consult with the laboratory.
 2. Do not allow the bottle to overflow when filling with sample.
 3. Leave a slight headspace in the bottle to allow for expansion of the sample.
 4. Cap the bottle securely and tape the cap to prevent it from working loose during shipping.
 5. Record the date and time of sampling on the bottle label and ASR form.

For tritium samples—Keep luminescent devices far from sample collection, handling, or storage areas.

5.6.3.1 Radon-222

Modify the sample collection setup to collect raw samples for radon analysis. Sample is collected in a glass vial containing liquid-scintillation solution (obtain radon kit from NWQL). Label radon-222 samples as "RUR-SV" and add the laboratory code.

**Do not write on or put any labels
on the side of the radon vial.**

Precautions are needed when collecting samples for radon analyses to prevent introducing gas bubbles into the sample and to prevent the sample from degassing.

- Use insulated sample tubing to prevent warming of the sample.
 - Inspect sample tubing to determine whether gas bubbles are forming inside the tubing or whether any air is being drawn into the sample at any connection.
 - Dislodge bubbles in sample tubing by striking the tubing firmly with a blunt object.
 - Tighten connections to help prevent entrainment of air.
 - To reduce degassing during sample collection, create back pressure by partially closing the valve on the radon-collection unit.
1. Collect the radon sample into a syringe directly from the pump discharge or other sampling device.
 2. Rinse the syringe as follows: Insert the glass syringe needle through the septum port with the collection-unit valve partially closed. Close the valve further until there is sufficient back pressure to create an almost effortless withdrawal of sample into the syringe. Fill the syringe partially, withdraw it from the septum and invert (needle up). Eject the water to waste. Repeat at least once.
 3. With the syringe plunger completely depressed (no air or water in the syringe barrel) and after the final rinse, reinsert the needle through the septum. Withdraw about 15 mL of sample into the syringe barrel slowly; avoid suction and degassing.

4. Withdraw the needle, invert the syringe (needle up), and eject the sample slowly until 10 mL remain in the syringe.
5. Tip the syringe needle downward, and insert the needle tip into the mineral oil and down to the bottom of the radon sample vial.
6. Inject the entire sample slowly. Remove the syringe and cap the vial firmly. Record the date and the exact time of sample collection on the top of the cap (do not write on or put a label on the vial).
7. Shake the vial for 30 seconds after injecting the sample. Repack it in the shipping tube and cap the tube. Complete the ASR form, wrap it around the tube, secure with a rubber band, and place the tube into a sealable plastic bag. **Ship to the NWQL immediately by overnight delivery. Do not ship samples on a Friday. Do not ship radon-222 samples in coolers.**

Do not allow air to contact samples for radon analysis.

Tritium/Helium-3 ($^3\text{H}/^3\text{He}$) 5.6.3.J

Refer to NWQL Technical Memorandum 97.04S for detailed information and instructions.

Do not allow air to contact samples for $^3\text{H}/^3\text{He}$ analysis.

Water samples for the helium determination are collected, in duplicate, in special pinch-off copper tubes that hold approximately 40 mL of water. These tubes are supplied through the NWQL but are the property of the analyzing laboratory (Lamont-Doherty Earth Observatory). Unused tubes must be returned to Lamont-Doherty. Notify NWQL of the number of tubes returned.

1. Set up the sampling apparatus. Collect the sample in duplicate. These samples must also be accompanied by 500 mL of sample in a glass or high-density polyethylene bottle for tritium analysis. In addition, archive a duplicate 500-mL sample.
 - a. Remove plastic caps covering the ends of the copper tube. **Handle the copper tube with care—damage to the ends from scratches and bends can prevent a good vacuum connection and thus compromise sample integrity.**
 - b. Connect the copper tube to the submersible pump discharge tubing.
 - Do not exceed 5 ft between the pump discharge and the sampling apparatus.
 - The connector to the pump-discharge tubing can be plastic, rubber, or metal, but it must be airtight.
 - Clear plastic tubing is preferred to allow visual inspection for possible air bubbles.
 - Airtight connections must not come loose when back pressure is applied during closing of copper tubes. Secure the connections with stainless steel hose clamps, placing clamps approximately 1 in. from the end of the copper tube. (Do not damage ends of copper tube.)
 - Attach a small valve to the discharge end of the copper tube and insert clear plastic (Tygon™) tubing to allow the operators to check for air bubbles (NWQL Technical Memorandum 97.04S provides photographs and diagrams).
2. Begin flow of the sample to the copper tube, checking for bubbles.
 - a. Hold the copper tube at a 45-degree angle, discharge up, while flushing bubbles from the system.
 - b. Forcibly tap the entire sample tubing and aluminum track that holds the copper tube with a socket wrench or other blunt object to dislodge gas bubbles. This typically takes about 1 minute.
3. Any backpressure to prevent formation of gas bubbles. Close valve until flow is reduced, tap channel, then close completely.
4. Seal the sample container.
 - a. Position the copper tube in approximate center of the pinch-off clamp.

- b. Use a socket wrench to close the bolts on the pinch-off clamps, starting at the discharge end.
 - c. Turn the bolts in successive order (back and forth approximately four times until firmly closed) so that the blades of the pinch-off clamp close approximately evenly.
 - d. Center the copper tube between the blades again, and close the pinch-off clamp on the inflow end as described in step c above.
 - e. Double check to ensure that all bolts are tight.
5. Repeat procedure above (1–4) to collect a duplicate sample.
 6. Disconnect the copper tube from the pump discharge tubing and remove the backpressure valve from the discharge end of the copper tube, taking care not to scratch or otherwise damage the ends.
 - a. If the sample is saline, acidic, or otherwise corrosive, wash the ends of the copper tube with DIW.
 - b. Take care not to bend the ends of the sealed copper tube.
 - c. Do not replace the plastic caps on the ends of the copper tube.
 - d. Place label onto the aluminum track of each sample—do not write on the tube. Include station identification, date, and time of sampling on the label.
 7. Prepare the sample(s) for shipment. Fill out a form or submit a letter to the analyzing laboratory with the following information:
 - Unique site identification number(s).
 - Date and time of sample collection.
 - Ground-water temperature at time of collection and recharge temperature, if known.
 - Estimated or known tritium concentration.
 - Estimated or known elevation of the recharge area for the sample.
 - General description of the hydrogeologic environment, location, and well-construction information.
 - Information regarding possible tritium contamination of the sample.
 - Name, fax number, E-mail address, and phone number of the person responsible for the sample(s).

5.6.3.K Chlorofluorocarbons (CFC-11, CFC-12, CFC-113)

Chlorofluorocarbons (CFCs) can be analyzed in samples of ground water, surface water, or air. The information that follows is summarized from the Office of Water Quality/Office of Ground Water Technical Memorandum 95.02 and, while generally applicable to all media, is focused toward collection of ground water for CFC analysis. Before collecting CFC samples, review this memorandum for more detailed information on field sampling, site selection, analysis requests, and applications of CFC analyses in environmental investigations. Important information for collecting CFC samples is also provided in Busenberg and Plummer (1992) and Plummer and others (1993).

Do not allow air to contact samples for CFC analysis.

- ▶ **The collection, transport, and storage of water samples without contamination is critical in order to reliably age-date waters containing CFCs.**
 - ▶ Contact the CFC laboratory (USGS, Reston, Va.) to arrange for training and to plan for CFC sampling. Remain in contact with the CFC laboratory throughout the planning, sampling, and analysis phases.
1. Schedule CFC sampling several months in advance, using the CFC request form (fig. 5-4), in order to
 - Reserve the sampling equipment. Special sampling apparatus is loaned to USGS study personnel who will collect water samples for CFC analyses and who have had the training required for CFC sampling.
 - Obtain the required number of borosilicate-glass ampoules (five ampoules per ground-water sample). The borosilicate-glass ampoules are supplied by the USGS CFC laboratory and are included in the price of analysis.
 - Obtain cylinders of compressed ultra-pure nitrogen gas and welding-grade oxygen.

2. Assemble additional tools, materials, and equipment needed (table 5-8; Office of Water Quality/Office of Ground Water Technical Memorandum 95.02).
 - Discuss the type and modification of pumping equipment with the CFC laboratory. USGS personnel should contact the laboratory in Reston, Va., by phone (703-648-5847), fax (703-648-5832), or E-mail (cfc@usgs.gov). The CFC laboratory will provide the guidance needed to prevent cross-contamination of samples collected contemporaneously for CFCs and trace elements.
 - Replace the sample discharge tubing with the appropriate tubing (table 5-8): refrigeration-grade copper or aluminum tubing are recommended; nylon tubing can be used but should be analyzed by the CFC laboratory before use; chromatographic-grade 304 stainless steel tubing also can be used. **Do not use fluorocarbon polymer tubing.**
3. Collect an equipment blank and submit for CFC analysis at least 1 week before collecting environmental samples.
 - For CFC sampling only, the matrix of the blank typically is water collected from a relatively deep well tapping an aquifer recharged only with pre-1940 water.
 - Ship the sample by overnight delivery to the USGS CFC Laboratory in Reston, Va.
 - Review QC-data results and make equipment changes accordingly. Proceed with sampling only if the equipment blanks are clean.
4. Collect preliminary samples for radiochemicals and VOC analyses at the well(s) selected (steps 5a through c below) and review the results before collecting or submitting the samples for CFC analyses. Select wells that are open hole or have metal or threaded (not glued) PVC casing. **Do not submit samples for CFC analyses that contain the following:**
 - Hazardous radioactive substances.
 - More than 0.5 mg/L of any CFC or other halocarbon (vinyl chloride, methyl chloride, methyl chloroform, methyl bromide, methylene chloride, chloroform, trichloroethylene, carbon trichloride, and tetrachloroethylene).

5. Sample collection.
 - a. Review sampling plans.
 - b. Measure the water level and prepare to purge the well. +
 - c. Purge the well, recording field measurements for specific electrical conductance, pH, temperature, and dissolved oxygen at approximately 5-minute intervals (NFM 4.2; NFM 6).
 - **The measurement of dissolved-oxygen concentrations is particularly important.**
 - **Record on field forms whether or not a hydrogen sulfide odor is detected.** Collect the samples needed for other organic and inorganic analyses. **Collection of samples for analysis of VOCs and tritium is strongly recommended when collecting samples for CFC analysis.**
 - d. Set up the CFC sampling equipment. Replace the sample tubing, if necessary, or make adjustments to direct the sample flow through copper lines or other appropriate tubing.
 - **CFC samples must not come in contact with air.** Use only the CFC apparatus specifically designed for this purpose that is supplied by the CFC Laboratory.
 - Review the precautions listed for radon sampling (section 5.6.3.I) to prevent sample degassing and air contact.
 - e. **Collect ground water into a borosilicate-glass ampoule—you will need five ampoules per well.** Flame-seal the ampoule. Repeat for each of the remaining ampoules. (It takes about 5 minutes to collect sample into an ampoule.) +
 - Follow the instructions given in training for site evaluation and use of the CFC sampling apparatus.
 - After the last ampoule is filled and sealed, measure specific electrical conductance, pH, temperature, and dissolved oxygen and record the measurements on the field form.

+

- +
6. Determine, if feasible, concentrations of hydrogen sulfide and methane, tritium/helium-3, and dissolved nitrogen and argon gases.
 - a. Measure hydrogen sulfide concentrations (Baedecker and Cozzarelli, 1992) if there is a hydrogen sulfide odor.
 - b. Collect sample for tritium/helium-3 age dating.
 - c. Collect sample for analysis of dissolved nitrogen and argon gases (to determine temperature of recharge water) and arrange for dissolved gas analyses. USGS personnel should contact the Northeastern Region Common Use Laboratory at (703) 648-6234.
 7. Label the sample ampoules as directed by the CFC Laboratory. Pack the ampoules in the boxes supplied by the CFC Laboratory (place padding on top of the ampoules). Be sure to pack the field form (fig. 5-4) in the box with the ampoules.
 8. **Ship the CFC samples to arrive the next day**, from Monday through Thursday. Do not ship on a Friday; there must be no weekend overlay of samples.
- +
- +

USGS Chlorofluorocarbon Laboratory
Reston, VA 20192

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REQUEST FOR CFC SAMPLING EQUIPMENT AND ANALYSIS

Today's date: _____ Name of contact: _____

Phone: _____ E-Mail: _____

FAX: _____

Description of job (where? project? purpose of CFC dating?):

Shipping Address: _____

Account number for billing: _____

Dates of sampling: _____

When to ship equipment:

Date equipment and ampules will be returned to CFC lab:_____

Number of wells: _____

Well/Source: ☐ monitor; ☐ domestic; ☐ municipal; ☐ spring; ☐ other

Well diameters: 2 in.; 4 in.; 6 in.; other: _____

Range of well depths: _____ feet

Materials of well construction: ☐ PVC; ☐ metal; ☐ other

Pump to be used: _____

Figure 5–4. Request form for equipment, instructions, and analysis of chlorofluorocarbon samples.

REQUEST FOR CFC SAMPLING EQUIPMENT

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AND ANALYSIS, *Continued*

Material of discharge tubing of pump: _____

Equipment normally provided by laboratory includes CFC sampler,
 spare parts, CFC trap, ampoules, ampoule holder.

Do you also need:

Garden-hose connector to well? _____

Other? _____

Are dissolved gases to be sampled? _____ Contact 703-648-6234 or

E-mail cfc@usgs.gov).

Which gases? _____

How many? _____

Will surface water be collected for CFC analysis? _____

How many samples and (or) stations? _____

Will air samples be collected for CFC analysis? _____

How many samples and (or) stations? _____

Do you need training on CFC sampling procedures? ____yes; ____no

Do you need the CFC laboratory to send personnel to help with training or
 sampling? ____yes; ____no

Contacts and address for Reston CFC laboratory:

U.S. Geological Survey

E-Mail: cfc@usgs.gov

432 National Center

Phone: 703-648-5838

12201 Sunrise Valley Drive

FAX: 703-648-5832

Reston, VA 20192

Figure 5-4. Request form for equipment, instructions, and analysis of
 chlorofluorocarbon samples—*Continued*.

Table 5-8. Equipment and supplies used for collection of samples for chlorofluorocarbon analysis

[CFC, chlorofluorocarbon; %, percent; MAPP, methyl acetylene-propadiene + petroleum gas (liquefied); QW Tech Memo, Office of Water Quality Technical Memorandum 95.02]

Item	Description	Source
CFC sample apparatus and ampoules	Refer to Busenberg and Plummer (1992). Return unused ampoules to the laboratory. Check with CFC laboratory for pump type, fittings, and special connectors needed.	CFC Laboratory, USGS, MS 432, Reston, VA 20192 or E-mail cfc@usgs.gov
Field gases Ultra-pure nitrogen Welding-grade oxygen MAPP gas or propane	Two C-size tanks. Carrier grade 99.999% pure or better; one tank is used for backup. One C-size or two D-size tanks; or, cannisters for welding kit. Fuel gas, provided in a fully gaseous state.	Hardware or plumbing supplies
Sample tubing, fittings ¹ Copper, aluminum, or stainless steel Compression fittings (such as Swagelok) Nylon ¹ (copper or aluminum are preferred)	1/4-inch, refrigeration grade. Stainless steel: use chromatographic 304 grade. 1/4-inch, preclean to remove lubricating oils or special order without lubricating oils. 1/4-inch tubing; preclean as described for inorganic-constituent samples in NFM 3.	Plumbing supplies. For aluminum tubing, refer to QW Tech Memo 95.02 Hardware supplies, or special order Scientific suppliers
Torch and regulator equipment Welding kit (refer to description in QW Tech Memo 95.02) Oxygen regulator	Example: Bernzomatic™ Model OX2500 or equivalent (contains torch, hoses, valves for canisters of oxygen and fuel gases, spark igniter). Recommended for oxygen line.	Hardware suppliers If kit will not be used, have welding supplies assembled by a welding equipment store.
Field tools Wrenches, adjustable Pliers Screwdrivers Tubecutter Tape Spark igniter Wash bottle Metal file	12 inch (for attaching regulators to gas cylinders). 6-inch (for attaching gas and water lines). Allen wrench set (for sampler repairs). Needle-nose and standard. Phillips and standard. For 1/8-inch and 1/4-inch tubing. Fluorocarbon polymer (PTFE) and electrical. To light torch. 250 milliliter (for water to clean off sampler). To smooth the cut edges of metal tubing.	Hardware suppliers

¹**Materials not suitable for tubing:** Tygon, silicone rubber, most plastics (including fluorocarbon polymers), rubbers. Use only refrigeration-grade copper or aluminum tubing, as other grades have oil coatings inside. If using nylon tubing, send it to the CFC laboratory for analysis to confirm that it does not contain substances that might affect CFC analysis.